U. S. Department of Agriculture, Forest Service

FOREST PRODUCTS LABORATORY

In cooperation with the University of Wisconsin

MADISON, WISCONSIN

METHODS OF THE FOREST PRODUCTS LABORATORY FOR THE ANALYSIS OF CRUDE PYROLIGNEOUS ACID

NOT FOR PUBLICATION

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METHODS OF THE FOREST PRODUCTS LABORATORY FOR THE ANALYSIS OF CRUDE PYROLIGNEOUS ACID

Total acid

Place 5 or 6 glass beads or porcelain chips in a 200 or 300 cc. Jena or Pyrex distilling flask fitted with a two-hole rubber stopper. Weigh flask and beads without stopper. In one hole of the rubber stopper put a 100 cc. dropping funnel and in the other hole a 250°C. thermometer adjusted so that it touches the bottom of the flask. Pipette 100 cc. of the crude pyroligneous acid into the dropping funnel and place flask in a sand bath. The temperature of the sand bath should not exceed 225°C. The crude acid is distilled by dropping it into the flask, at a rate just enough faster than the rate of distillation to prevent the temperature as shown by the thermometer in the flask rising above 140°C. When all of the crude acid has been added place 50 cc. of distilled water in the dropping funnel and as soon as the thermometer in the flask reads 140°C. begin adding the water at the same rate used for the acid. The distillation is complete when all of the water has been added and the thermometer reads 150°C. Remove the

stopper at once and wipe the bulb of the thermometer on the inside of the neck of the flask to remove adhering tar. Remove flask from sand bath, wipe clean, let cool and weigh. The gain in weight of the flask is the grams of dissolved tar per 100 cc. of crude acid. Make up distillate to 250 cc., mix thoroughly and titrate a 50 cc. portion with normal sodium hydroxide, using phenolphthalein as indicator. The titration should be made cold with 6 or 7 drops of indicator. The end point is not very sharp and usually goes through a reddish-orange stage to a permanent red. The end point should be carried to the first permanent red; record as total acid. The titration should be made as soon as possible after distillation and must be made the same day as the distillation since there is usually considerable oxidation and darkening of the tar-free distillate, even on standing over night in a well stoppered flask, which makes the determination of the end point difficult.

Acetic acid

Add an excess (25 grams) of finely powdered mercuric oxide to 50 cc. of the distillate obtained in total acid determination. The mixture is made up to about 100 cc., well stirred and placed on a steam bath. At the end of two hours

enough more mercuric oxide is added so that the mercuric oxide precipitated in the bottom gives a layer of about 15 grams in weight. Allow to remain on the steam bath one hour longer. The total is then transferred to a 500 cc. distilling flask and an excess (40 cc.) of syrupy 85 per cent phosphoric acid is added (to decompose any mercuric acetate formed); also add a few drops of paraffin oil to prevent frothing. The mixture is distilled until a slight frothing is noticed, and the residue is washed by distillation with 100 cc. of water dropped in from a dropping funnel just fast enough to prevent frothing. The whole distillate is then titrated with normal sodium hydroxide, using phenolphthalein as indicator.

Calculations

cc. NaOH for Total Acid - cc. NaOH for Acetic Acid = cc. NaOH for Formic Acid.

$$\frac{5 \times \text{cc. alkali} \times .06033}{\text{sp. gr. pyro. acid}} = \% \text{ Acetic Acid}$$

$$\frac{5 \times \text{cc. alkali} \times .04602}{\text{sp. gr. pyro. acid}} = \% \text{ Formic Acid}$$

Wood alcohol

Measure 500 cc. of crude pyroligneous acid into a 1 liter distilling flask placed on an asbestos gauze. Distill over 300 cc.; make the distillate strongly alkaline with

strong sodium hydroxide[1] (35 to 40 per cent solution of commercial sodium hydroxide is satisfactory and 75 cc. is ample), and distill the neutralized distillate to a volume of 225 cc. The same flask used in the first distillation may be used for the second after simply emptying out the contents. A sand bath should be used for this distillation to permit complete hydrolysis of methyl acetate. Add to the second distillate an excess of the strong alkali used for the first distillate (10 cc. is sufficient) and distill over 65 per cent, corresponding to a volume of approximately 155 cc. A fourth distillation of 65 per cent should be made, adding about 2 cc. of concentrated sulphuric acid before making the distillation. The last distillation should be made with a well cooled condenser and 100 cc. collected in a volumetric flask. Five hundred cc. distilling flasks placed on asbestos gauze can be used for the third and fourth distillations. Glass beads or porcelain chips should be used in all distilling flasks to prevent bumping and frothing. The specific gravity of the distillate is obtained with a pycnometer at 15.56° C. and the volume should be adjusted to 100 cc. when the flask and its contents are at the temperature of 15.56°C. The per cent alcohol corresponding to a given density can be obtained from the table

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1 The dark color produced on adding the alkali prevents the use of litmus paper and phenolphthalein cannot be used on account of the alcoholic solution.

of Dittmar and Fawsitt (see Van Nostrand's Chemical Annual or Smithsonian Physical Tables). Mix the distillate thoroughly after adjusting the volume and before determining the density.

Calculations

$$\frac{\text{sp. gr. of final dist. x \% alcohol in final dist. x 100}}{\text{5 x sp. gr. of original pyro.}} =$$

% alcohol by weight in the pyro. acid.

Acetone

To a 25 cc. portion of the final alcohol distillate add 10 cc. of 2N sodium carbonate, then add 50 cc. of N/10 iodine, counting three minutes by a stop watch and beginning to count when the pipette is one-half empty. At the end of three minutes add 10 cc. of 3N H_2SO_4. The whole is then titrated with N/10 sodium thiosulphate, using starch as indicator. The difference between 50 and the number of cc. of thiosulphate used equals the number of cc. of iodine absorbed.

Calculations

$$\frac{\text{cc. iodine x .096672 x sp. gr. final dist. x 100}}{\text{25 x 500 x sp. gr. pyro. acid}} =$$

% acetone by weight in pyro. acid.

UNITED STATES DEPARTMENT OF AGRICULTURE

FOREST SERVICE

FOREST PRODUCTS LABORATORY

ADDRESS REPLY TO
DIRECTOR
AND REFER TO

RPL
Library

MADISON, WISCONSIN

May 28, 1929

Miss Emma B. Hawks, Associate Librarian,
United States Department of Agriculture Library
Washington, D. C.

Dear Miss Hawks:

We are pleased to give you an extra copy of "Methods of the Forest Products Laboratory for the Analysis of Crude Pyroligneous Acid" which is based upon a memorandum from Mr. R. C. Palmer, June 16, 1916. This typed report is enclosed.

No doubt, the person who requested this information has also consulted Department Bulletins 129 and 508 entitled, "Yields from the Destructive Distillation of Certain Hardwoods.

Very sincerely yours,

Ellen A. Hoffman
Librarian.

Enclosure:
1 report

U.S.D.A. Forest service. Forest products laboratory.
Methods...for analysis of crude pyroligneous acid. c1927.

1 mss. slip

Return to CT

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